Universal threshold law for ion-neutral-neutral three-body recombination

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A very recently method for classical trajectory calculations for three-body collision [J. Pérez-Ríos, S. Ragole, J. Wang and C. H. Greene, J. Chem. Phys. **140**, 044307 (2014)] has been applied to describe ion-neutral-neutral ternary processes for low energy collisions: 0.1 mK - 10 mK. As a result, a threshold law for the three-body recombination cross section is obtained and corroborated both, experimentally and numerically. The derived threshold law predicts the formation of weakly bound dimers, with binding energies comparable to the collision energy of the collisional partners. In this low energy range, this analysis predicts that molecular ions should dominate over molecular neutrals as the most products formed.

I. INTRODUCTION

A nonradiative collision of two atoms cannot lead to the formation of a stable molecule, due to the conservation of energy (it can lead to the formation of a transient resonant state). Nevertheless, three atoms can collide and eventually, form a molecule *i.e.* $A + A + A \rightarrow A_2 + A$. This is the three-body recombination (TBR) process. TBR processes are one of the main loss mechanisms in systems of ultracold atoms, often dominant in Bose-Einstein condensates.[1–8] Recently, the development of hybrid traps technology, where both neutrals and ions overlap in the same spatial region,[9–15] has opened the possibility to study ion-atom interactions and different chemical processes attached to them. These studies have revealed a rich chemistry at such cold temperatures mainly due to charge transfer reactions. However, it has been observed that in high density environments, the chemical reactions are dominated by three-body recombination processes.[16] These TBR processes involving neutrals and charged particles have received comparatively little theoretical interpretation.[17–19] In particular, there has been no available prediction concerning the final product states and the dependence of the TBR cross section as a function of the collision energy.

The present study reports the derivation of a first principles classical threshold law for ion-neutral-neutral TBR. This threshold law is numerically tested by comparing its predictions with the numerical results coming from classical trajectory calculations,[20] as well it is experimentally observed in hybrid trap experiments.[21] The derived threshold law for the TBR cross section shows a power law behavior on the collision. This also has fundamental implications for the final product states for an ion-neutral-neutral, which we demonstrate to be fully dominated by the formation of molecular ions instead of neutral molecules.

II. RESULTS

For any two-body interaction, the power-law long-range tail of the potential establishes a length scale, and associated with it an energy scale.These scales define the range where the collisions exhibit a totally quantal nature. In particular, for most types of neutral atom-atom interactions, in particular for S-wave ground state atoms, the long-range potential is dominated by the van der Waals interaction. In that case, the length scale is defined as $2R_{vdW} = (2\mu C_6/\hbar^2)^{1/4}$, and the energy scale as $E_{vdW} = \hbar^2/(2\mu R_{vdW}^2)$, referred to as the van der Waals length and van der Waals energy, respectively.[22] For alkali-alkali collisions one typically finds $R_{vdW} \sim 100$ a_0 and $E_{vdW} \sim 1$ mK. However, for ion-atom interactions, the long-range is dominated by the charge induced dipole moment interaction $-C_4/r^4$, where $C_4 = \alpha/2$, and α is the neutral atom polarizability. For this case, we define the polarization length $R_\alpha = (\mu\alpha/\hbar^2)^{1/2}$ and the polarization energy as $E_\alpha = \hbar^4/(2\mu^2\alpha)$. Typically for ion-alkali atom interactions these values are of order $R_\alpha \sim 5000$ a_0 and $E_\alpha \sim 100$ nK, in particular for Rb - Rb^+ and for Ba^+-Rb are 156 nK and 104 nK, respectively. Therefore, cold collisions (in the milikelvin range) involve many partial waves. For this reason, classical trajectory calculations are expected to be reasonably accurate for revealing the reaction dynamics in hybrid trap experiments. In particular, Newtonian mechanics should be applicable for the study of ion-neutral-neutral TBR processes.

A recently developed method for the calculation of TBR cross sections based on classical trajectories[20] has been adapted for the study of ion-atom-atom recombination. The method employed relies on mapping the three-body problem into a 6-dimensional space (after separating out the trivial center of mass motion), where the cross section emerges as a generalization of the well-known two-body cross section.[20] Hyperspherical coordinates[23] are used for representing the positions and momentum vectors in the 6-dimensional space leading to a very efficient sampling of the phase-space. In hybrid trap experiments, the kinetic energy of the ion is almost two orders of magnitude higher than the energy of the ultracold neutral atoms. Keeping this in mind, the classical trajectory calculations (CTC) presented here have been performed by fixing one of the hyperangles associated with the initial momentum, guaranteeing that 95 % of the collision energy is associated with the kinetic motion along the

direction of the ion. However, general CTC without any constraint have been also performed and they will denoted as FCTC in the present work.

Figure 1 displays our results for the TBR cross section for $^{87}Rb^+$ -^{87}Rb -^{87}Rb, and for $^{138}Ba^+$ -^{87}Rb -^{87}Rb, which are presented in panels (a) and (b), respectively. The TBR cross section for the systems at hand has been computed by running 10^5 trajectories per collision energy. During the simulation the energy is conserved up to the fifth decimal place, and the same is observed for the angular momentum. Details about the numerical method employed to solve Hamilton's equations of motion, in conjunction with the sampling of the initial conditions, can be found elsewhere.[20] All of the calculations have assumed that neutral-neutral interactions, as well as ion-neutral interactions occur along one single potential energy curve. Concretely, Rb - Rb collisions are assumed to occur through the $^3\Sigma$ potential, *i.e.*, the spin flip transitions have been neglected. In particular, the potential of Strauss *et al.* has been employed.[24] On the other hand, the ion-neutral potential is described by the model potential $-C_4(1-(r_m/r)^4/2)/r^4$, where C_4 denotes the experimental long-range coefficient of the interaction, which is taken as C_4=160 a.u. along this work, and r_m represents the position of the minimum of the potential. For Ba^+ - Rb interaction the value of r_m is taken from the work of Krych *et al.*[25], whereas for Rb^+ - Rb the same magnitude comes from Jraij *et al.*[26]

Fig. 1 shows that the TBR cross section for the systems depends quite smoothly on the collision energy, which is independent of the nature of the system at hand; this suggests an emerging universal threshold behavior. Figure 1 (b) demonstrates that the constraint in the hyperangles associated with the momentum (CTC) does not affect the general trend of the TBR cross section, as good agreement is seen with the FCTC results. This suggests that the emerging threshold behavior is largely independent of the initial momentum vectors of the system. In other words, the dependence of the TBR cross section must be primarily controlled by the interatomic potential among the involved particles. In order to emphasize the dependence of the TBR cross section on the collision energy, the power law fits of the CTC results are shown as dashed lines, and the fitting parameters are presented in Table I.

For low energy collisions, particles probe the long-range tail of the interaction during most of the collision time. The case of ion-atom-atom collisions is not an exception, but it requires some special consideration in the three-body recombination system of interest here, since there are two different long-range potentials involved in the problem, namely atom-atom and ion-atom. From a long-range perspective, the ion-atom interaction is of course far more attractive than the atom-atom interaction. For any orientation, energy and impact parameter, the collision begins when the trajectories of the atoms start to deviate from uniform rectilinear motion. This occurs when the interaction potential where

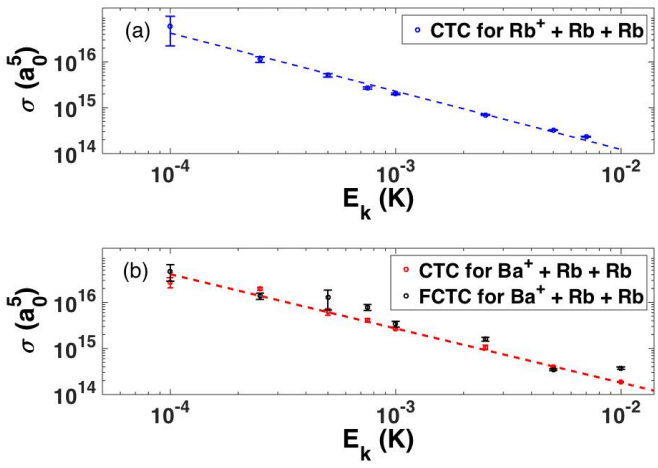

FIG. 1. (color online). Three-body recombination cross section (in a_0^5) as a function of the collision energy (in K). Panel (a) $^{87}Rb^+$ - ^{87}Rb - ^{87}Rb ; the circles represent the numerical results by means of CTC whereas the dashed line stands for the fitting of the points. Panel (b) $^{87}Rb^+$ - ^{87}Rb - ^{87}Rb ; red circles represent the numerical results by means of CTC, the black circles denote the results using CTC without any constrain on the (see text for details), the dashed line stands for the fitting of the obtained CTC results. The fitting function assumed for both systems is $\sigma(E_k) = \gamma E_k^{\beta}$, and the results are presented in Table I.

the moving atoms are currently located is comparable to the collision energy, *i.e*, $E_k \approx C_4/r^4$. Here, we will assume that this value of the radius defines the maximum impact parameter associated to a TBR event, *i.e.* $b_{max}(E_k) = (C_4/E_k)^{1/4}$. In the present formalism the TBR cross section is defined as[20]

$$\sigma(E_k) \propto \int_0^{b(E_k)_{max}} b^4 db, \qquad (1)$$

where a unit opacity function has been assumed. Finally, taking into account the expression for $b_{max}(E_k)$ and substituting it in Eq. 1, $\sigma(E_k) \propto E_k^{-5/4}$ it is found. This result is compared in Fig.1 with a fit of the CTC numerical results shown in Table I. In particular, the fitting function employed has the form $\sigma(E_k) = \gamma E_k^{\beta}$, where β is related with the energy scaling law associated with the TBR cross section at low energies, which reveals the underlying classical threshold law. The errors reported in Table I are associated with a confidence interval of 95 %.

In Table I, it is observed that energy scaling law for the TBR cross section numerically obtained for both systems, $^{87}Rb^+$ - ^{87}Rb - ^{87}Rb and $^{138}Ba^+$ - ^{87}Rb - ^{87}Rb, are in a good agreement with the predicted energy scaling law associated with the derived threshold law. This suggests that the derived threshold law is satisfied in different systems under different dynamical conditions. A similar threshold law was derived and numerically confirmed

TABLE I. Classical threshold law for the TBR cross section. A power law dependence of the TBR cross section as a function of the collision energy is assumed and used as a fitting function for the CTC numerical results presented in Fig. 1. The error on the fitting parameters are associated with a confidence interval of 95 %.

System	γ (a_0^5)	β (dimensionless)
$^{87}Rb^+$ - ^{87}Rb - ^{87}Rb	(7.94 ± 2.72) 10^{11}	-1.178 ± 0.068
$^{138}Ba^+$ - ^{87}Rb - ^{87}Rb	(3.57 ± 0.07) 10^{11}	-1.269 ± 0.132
Classical threshold law		-1.25

for atom-atom-atom collisions.[20] On the other hand, the presented results for $^{138}Ba^+$ - ^{87}Rb - ^{87}Rb have been corroborated in hybrid trap experiments, yielding a first principles explanation of the observed ion losses caused by TBR processes.[21]

The derived threshold analysis has implications beyond the energy dependence of the TBR cross section. It predicts that the final molecular product states will be weakly bound. This is due to the correlation between the collision energy and to the binding energy, which has been observed in previous calculations[20] for neutral-neutral-neutral TBR processes, and confirmed in the present calculations for ion-neutral-neutral TBR. Moreover, the CTC and FCTC calculations both establish that molecular ions constitute the dominant product channel. This may be associated with the dominance of the of the ion-neutral long-range interaction on the cross section.

III. CONCLUSIONS

A classical threshold law for ion-neutral-neutral TBR processes has been derived, numerically confirmed, and also experimentally corroborated. The present threshold behavior apart from the prediction of the energy dependence of the TBR cross section, has significant implications in terms of the expected reaction products. In particular, the low energy threshold law for TBR involving one charged particle and two neutrals predicts that predominantly molecular ions are formed as products of the TBR. This might seem counterintuitive, since in principle one expects some influence of the atom-atom interaction on the dynamics. However, as is discussed above, the ion-atom interaction presents a more attractive nature than the atom-atom, and hence it dominates the dynamics of the collision. Nevertheless, it has been checked that the situation changes as the collision energy increases. In that case, the atom-atom interaction eventually becomes as important as the ion-atom interaction.

The observation of molecular ions in hybrid traps will be quite challenging due to the presence of electric fields. In particular, weakly bound molecular ions are easily dissociated in the the Paul trap by the external electric field. For instance, with an electric field $\sim$ 1V/cm the molecular ion will dissociate on a time scale $\sim$ 100 ns (the time scale of the vibrational period). Sorting out the three-body reaction is also challenging because many of the reactions occur in the presence of the dipole trap light or MOT light. This light can couple the very weakly-bound vibrational states with highly excited states of the molecular ion, leading to far richer chemical processes involving excited states.

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